

# Electrochemical Copolymerization of Pyrrole and Thiophene Nanofibrils Using Template-Synthesis Method

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**ABSTRACT:** Copolymer nanofibrils composed of pyrrole and thiophene were prepared by synthesizing the desired polymer within the pores of microporous anodic aluminum oxide (AAO) template membranes. The copolymer nanofibrils were photographed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for microstructure analyses. The results of the SEM and TEM revealed that the copolymer nanofibrils obtained had uniform and well-aligned arrays and their diameter and length could be controlled by changing the aspect ratios of the AAO membrane. The results of cyclic voltammetry and IR

spectrometry indicated that polypyrrole and polythiophene were both involved in the copolymer. The nanofibrils that were obtained were identified as copolymers rather than composites. The influence of the applied polymerization potential on the synthesis of copolymer nanofibrils was investigated. The higher potential favored the incorporation of thiophene units into the copolymer nanofibrils. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2403–2407, 2002

**Key words:** electrochemical copolymerization; pyrrole; thiophene; template-synthesis method

## INTRODUCTION

Electronically conductive polymer nanostructures have recently caused a great deal of excitement in the physics, chemistry, and materials science communities.<sup>1–3</sup> Such nanostructures are inherently intriguing chemical systems and have myriad proposed technological applications.<sup>4,5</sup> The general synthetic route for preparing electronically conductive polymer nanostructures involves the template-synthesis method. This method entails the synthesis of a desired material within the pores of a microporous membrane. The membranes employed have cylindrical pores with monodisperse diameters. A tubule or fibril of the desired material is obtained within each pore. The template-synthesis method is used to prepare nanotubes or fibrils of electronically conductive polymers, metals, semiconductors, and carbon.<sup>6–10</sup> Because the aspect ratios of the nanostructures prepared via this method can be controlled at will, this template approach is proving to be a versatile method for the synthesis of nanomaterials.

Although a number of nanotubes or fibrils of electronically conductive polymers were prepared using the template-synthesis method, there are no known reports on the preparation of copolymers. We recently employed the chemical copolymerization technique for pyrrole and aniline loading and investigated the

structure and morphology of the copolymer fibers.<sup>11</sup> The main motivation for preparing such copolymers lies in the possibility that these materials will display better properties and help to overcome the limitation of the scarcity of new conjugated monomers that contain  $\pi$  bonds. Consequently, it becomes possible to select individual monomers having superior properties that polymerize in different environments and combine them.<sup>12</sup>

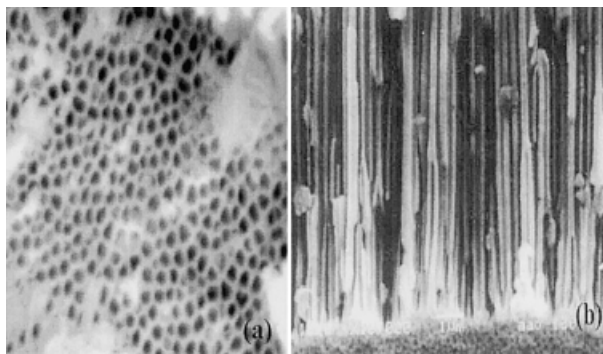
The present article reports the achievement of electrochemical copolymerization of pyrrole and thiophene from a mixture of each monomer. We employed the uniform and straight channels of an anodic aluminum oxide (AAO) membrane as a template. The oxidation potentials of these monomers are quite different. The copolymerization strategy that we employed is according to the method established by Kuwabata et al.,<sup>1</sup> in which the oxidation current of pyrrole at high polymerization potential is controlled by an extremely low concentration of pyrrole compared to that of thiophene. Thus, the technique reported in this article has scientific implications in giving a new route for copolymerizing two kinds of simple monomers whose oxidation potentials are far apart and we believe it to be widely applicable to the preparation of a variety of copolymer nanofibrils.

## EXPERIMENTAL

### Materials

Pyrrole and thiophene were purchased from Acros Chemical Co. and distilled under reduced nitrogen

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**Figure 1** SEM images of (a) the top surface structure and (b) the cross section of the AAO template membrane.

prior to use. Acetonitrile was purified according to the literature.<sup>13</sup> Tetraethylammonium perchloric acid ( $\text{Et}_4\text{NClO}_4$ ) was dried under a vacuum at  $100^\circ\text{C}$  for 24 h. All other ingredients were analytical grade and used without further purification.

### Procedures and measurements

#### Preparation of aao membranes

The AAO membranes were prepared by anodic oxidation of an electropolished aluminum plate at a cell voltage of 80 V in 0.5M phosphoric acid at  $25^\circ\text{C}$  for 1.5 h. The details of this method are described elsewhere.<sup>14</sup> We prepared the AAO membranes with a broad range of pore diameters and thicknesses by controlling the applied potential of the anodic oxidation and the oxidizing time. Consequently, the diameter and the length of the desired copolymer nanofibrils can be determined by the diameter and thickness of the AAO membranes. As indicated in Figure 1(a), the pores in the membrane are arranged in a regular hexagonal lattice. Figure 1(b) depicts the cross section of the AAO template with the pores parallel to each other and perpendicular to the surface of the membrane. The AAO membrane used in this study consisted of an array of parallel and straight channels with a diameter of about 100 nm, and the membrane diameter and its thickness were 15 mm and  $\sim 10\ \mu\text{m}$ , respectively.

#### Preparation of copolymer nanofibrils

Fibrillar polypyrrole, polythiophene, and polypyrrole/polythiophene copolymers were prepared by electrochemically synthesizing the polymers within the pores of the AAO membrane. In order to synthesize polymers into each of the pores, one surface of the AAO membrane must be converted into an electrode. This was accomplished by sputtering a thick layer of Au onto one face of the AAO membrane. Silver epoxy (Epotech 410-E) was used to attach a Au sheet to this

Au surface of the AAO membrane. The membrane/Au/Au sheet was used as a working electrode and only a  $0.5\ \text{cm}^2$  area of the AAO membrane was left exposed.

All electrochemical measurements were performed using a CHI660 potentiostat and were controlled by the CH instrument electrochemical software. The experiment was made in a one-compartment cell using a standard three-electrode cell arrangement with a membrane/Au/Au sheet working electrode, a platinum-wire counterelectrode, and an  $\text{Ag}^+/\text{Ag}$  reference electrode.

Scanning electron microscopy (SEM) images of the copolymer nanofibrils were obtained as follows: one surface layer was removed by simply polishing the surface of the membrane with  $1\text{-}\mu\text{m}$  alumina powder, and the membrane was epoxy glued to a piece of glass with the polished face up. The resulting composite was immersed in a 6M NaOH solution for 10 min to dissolve the AAO membrane. A JSM-5600LV electron microscope was used. The copolymer nanofibrils were sputtered with  $\sim 10\ \text{nm}$  of Au prior to SEM imaging.

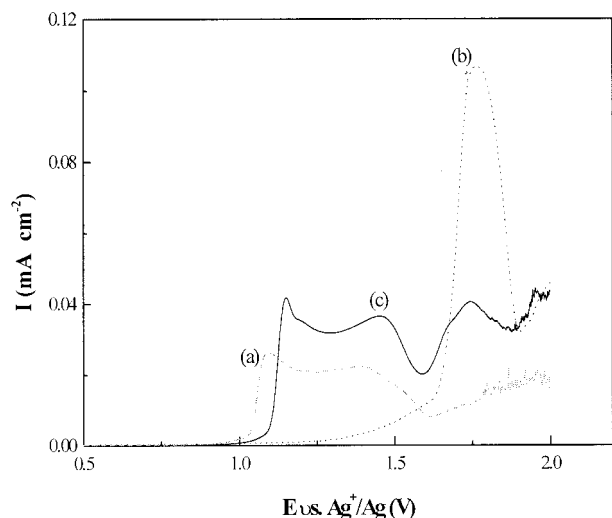
Transmission electron microscopy (TEM) images of the samples were obtained as follows: both surface layers were removed, and a piece of the resulting membrane was placed onto a carbon membrane coated TEM grid. The 6M NaOH solution was then applied to the membrane to dissolve the alumina. The freed copolymer nanofibrils were imaged using a Hitachi 600 electron microscope. The accelerating voltage of the electron beam was 100 kV.

The IR spectra were obtained by using a Nicolet AVATAR-360 Fourier transform IR (FTIR) spectrometer. Because the alumina had no absorption above  $600\ \text{cm}^{-1}$ ,<sup>15</sup> the AAO membrane was not dissolved with the 6M NaOH solution. The FTIR spectra showed only the absorption of the copolymer.

## RESULTS AND DISCUSSION

### Preparation of copolymer nanofibrils of pyrrole and thiophene

According to the literature,<sup>16</sup> electropolymerization of pyrrole occurs at a positive potential of 0.6 V versus a standard calomel electrode (SCE) and that of thiophene occurs at a positive potential of 1.6 V versus the SCE, the oxidation potentials being quite different for them. The copolymerization strategy employed in the present study was according to the method of Kuwabata et al.,<sup>1</sup> which was to oxidize pyrrole under diffusion limiting conditions at potentials where thiophene oxidation takes place. For this purpose, we arbitrarily chose a concentration of pyrrole as low as  $2.0 \times 10^{-3}\ \text{M}$  and that of thiophene was set at 0.1M. Acetonitrile was used as a solvent and 0.1M  $\text{Et}_4\text{NClO}_4$  was used as a supporting electrolyte.



**Figure 2** Current-potential curves of (a)  $2.0 \times 10^{-3}$  M pyrrole, (b) 0.1M thiophene, and (c)  $2.0 \times 10^{-3}$  M pyrrole and 0.1M thiophene in acetonitrile solution containing 0.1M  $\text{Et}_4\text{NClO}_4$  at a scan rate of 10 mV/s.

The current-potential curves taken in quiet solutions at a potential sweep rate of  $10 \text{ mV s}^{-1}$  are given in Figure 2. The measurements were carried out with ascending anodic potentials. It should be noted that the background electrolyte is electrochemically silent in the whole potential range. Curve a in Figure 2 presents a current-potential curve for electropolymerization of  $2.0 \times 10^{-3}$  M pyrrole. The diffusion limiting current shown in the figure does not parallel the potential axis but varies a little, which is due probably to changes in the electrode environments, such as the electrode roughness caused by successive deposition of polypyrrole. On the other hand, the current-potential curve became rough when the prepared potential increased above 1.8 V versus  $\text{Ag}^+/\text{Ag}$ , indicating that some restructuring of the polypyrrole is taking place.<sup>17</sup> When the polypyrrole nanofibrils were prepared in this solution at 2.2 and 1.5 V versus  $\text{Ag}^+/\text{Ag}$ , the resulting polymer nanofibrils showed almost the same cyclic voltammograms, suggesting that the electrochemical properties of the polypyrrole nanofibrils are not appreciably influenced by the potentials chosen for the polymerization of pyrrole. The current-potential curve taken in a 0.1M thiophene solution under the same conditions is shown in curve b in Figure 2. When a current-potential curve was taken in an acetonitrile solution containing  $2.0 \times 10^{-3}$  M pyrrole and 0.1M thiophene, curve c was obtained, which is regarded as a superposition of curve a on curve b in Figure 2. However, curves a and b in the figure do not strictly add up to curve c. This may be partly due to some change in the electrode environment caused during the course of I-E curve measurements and partly

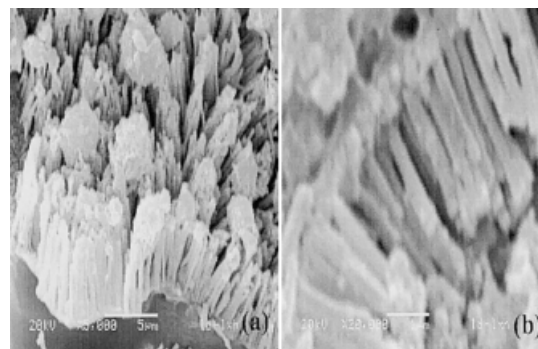
due to a contribution of the IR drop that is expected to be greater for copolymer films.

As shown below, the prepared polymers are copolymers, not mixtures of polypyrrole and polythiophene. Accordingly, the term copolymer is used below.

### Morphology of copolymer nanofibrils

Figure 3 shows the SEM images of copolymer nanofibrils composed of polypyrrole and polyaniline at low and high original magnifications. The AAO membrane was dissolved to expose the copolymer fibers prepared in the pores. This yields an ensemble of copolymer nanofibrils that protrude from the epoxy surface like the bristles of a brush. Some residual copolymer surface layers are observed at the tops of these fibers. Note the high density of fibrils; this reflects the very high porosity of the AAO template membrane. As would be expected, the fibril diameter is equivalent to the pore diameter (100 nm) of the template membrane. The lengths of these fibrils show that they span the complete thickness of the template. Figure 4 shows the TEM images of copolymer fibrils. The image exhibits the presence of uniform copolymer nanofibrils with diameters of 100 nm. Some fibrils clump together because of physical adsorption on the surface of the fibrils.

The template-synthesis method yielded either tubules or fibers of the desired copolymer within the pores of the AAO membrane by controlling the polymerization time and temperature. As a result, polymeric tubules are obtained at short polymerization times, although they are not shown here. When the copolymers are synthesized electrochemically within the pores of the AAO membrane, the copolymer preferentially nucleates and grows on the pore walls.<sup>3,7</sup> This is attributed to the fact that the polymers are cationic and there are anionic sites on the pore wall of the AAO membrane.



**Figure 3** SEM images of copolymer nanofibrils at (a) low and (b) high original magnifications.

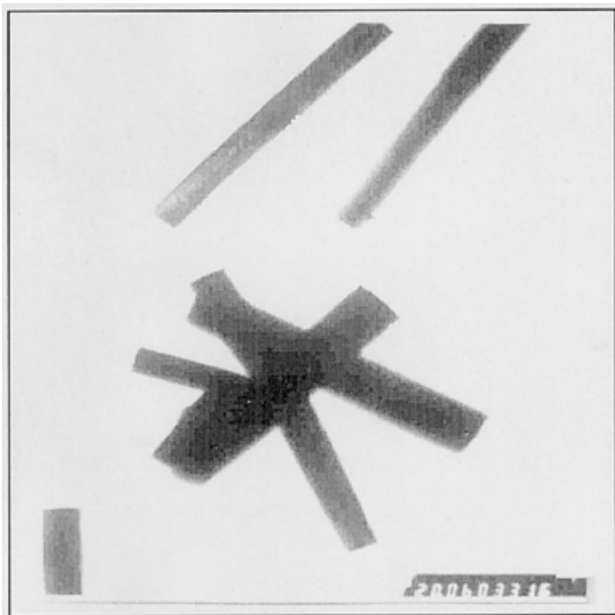


Figure 4 A TEM image of the copolymer nanofibrils.

### Cyclic voltammetry

The copolymerization is performed under potentiostatic conditions. Figure 5 shows a typical cyclic voltammogram of the copolymer nanofibrils obtained in an acetonitrile solution containing  $2.0 \times 10^{-3}$  M pyrrole and 0.1M thiophene and prepared at 1.8 V versus  $\text{Ag}^+/\text{Ag}$ , together with that of pure polypyrrole and pure polythiophene. Only one anodic/cathodic peak current couple appears in the copolymer nanofibrils, which is quite different from that of polypyrrole and

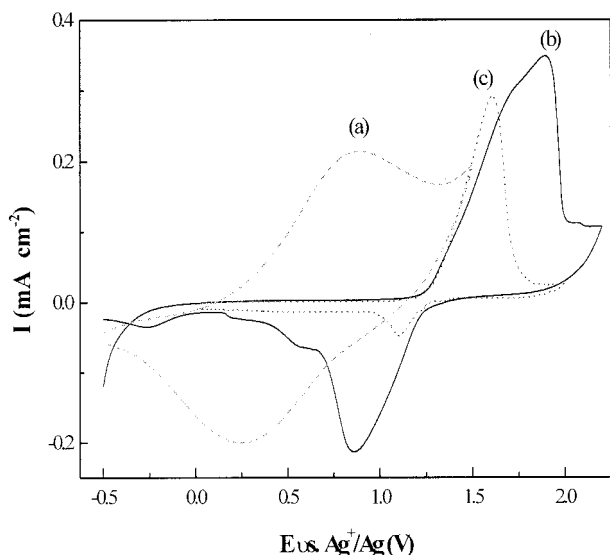


Figure 5 Cyclic voltammograms of (a) pure polypyrrole, (b) pure polythiophene, and (c) the copolymer nanofibrils prepared at 1.8 V versus  $\text{Ag}^+/\text{Ag}$  recorded in acetonitrile solution containing 0.1M  $\text{Et}_4\text{NClO}_4$  at a scan rate of 100 mV/s.

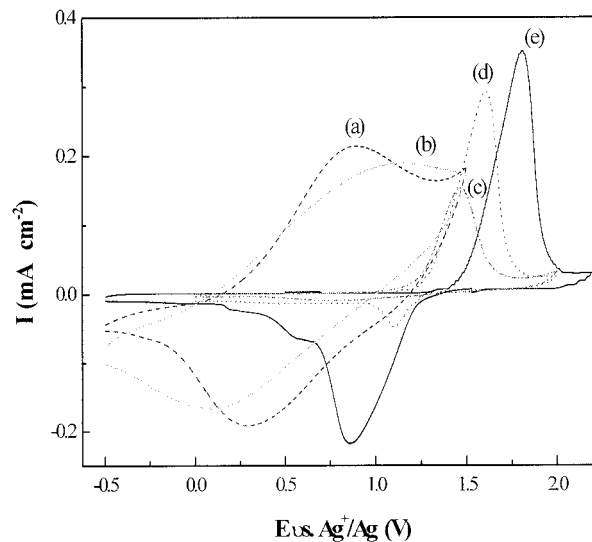


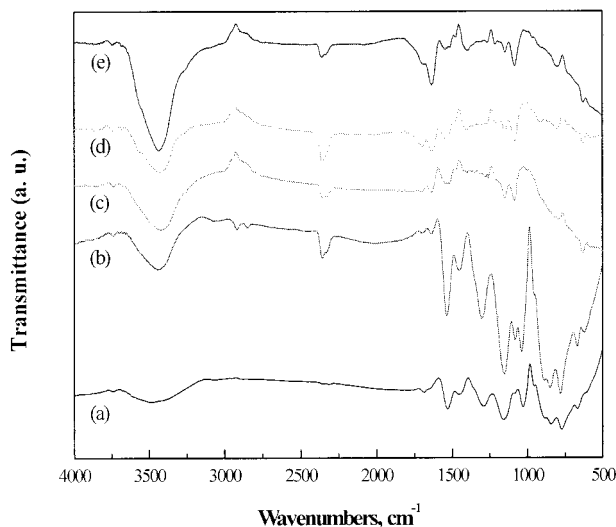
Figure 6 Cyclic voltammograms of the copolymer nanofibrils prepared at (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.0 V versus  $\text{Ag}^+/\text{Ag}$  recorded in acetonitrile solution containing 0.1M  $\text{Et}_4\text{NClO}_4$  at a scan rate of 100 mV/s.

polythiophene as in the case of a copolymer of pyrrole and *N*-methyl pyrrole.<sup>18,19</sup> If the prepared copolymer nanofibrils were mixtures of polypyrrole and polythiophene, two couples of anodic/cathodic peak currents due to the redox reactions of polypyrrole and polythiophene should have appeared at different potentials. Thus, the appearance of one redox peak couple of the copolymer nanofibrils indicates that the polymers are copolymers of pyrrole and thiophene.

The electrochemical copolymerization at different potentials was investigated. Figure 6(a-e) shows the cyclic voltammograms of the copolymer nanofibrils obtained in an acetonitrile solution containing  $2.0 \times 10^{-3}$  M pyrrole and 0.1M thiophene at potentials ranging from 1.2 to 2.0 V versus  $\text{Ag}^+/\text{Ag}$ , respectively. An interesting characteristic of the cyclic voltammograms is that the anodic peak potential of the copolymer nanofibrils shifts to higher potentials with the increasing preparation potential for the copolymer. When prepared at 1.2 V, the copolymer shows an anodic peak at 0.8 V, which is very similar to that of pure polypyrrole; when prepared at 2.0 V, the copolymer shows an anodic peak at 1.9 V, which is close to the redox peak of pure polythiophene. This indicates that more thiophene units are incorporated into the copolymer with the increased preparation potential.

### IR spectra

The FTIR spectra of pure polypyrrole, pure polythiophene, a mixture of polypyrrole and polythiophene, and the copolymer nanofibrils prepared at 1.5 and 1.8 V versus  $\text{Ag}^+/\text{Ag}$  are shown in Figure 7. As expected, the shapes and positions of the absorption bands of



**Figure 7** IR spectra of (a) pure polypyrrole, (b) a mixture of polypyrrole and polythiophene (1:1), (c) copolymer nanofibrils prepared at 1.5 V, (d) copolymer nanofibrils prepared at 1.8 V versus  $\text{Ag}^+/\text{Ag}$ , and (e) pure polythiophene.

the mixture of polypyrrole and polythiophene are constituted by those observed from polypyrrole and polythiophene, whereas the spectrum of the copolymer is different from that of the mixture. The most impressive characterization difference in the copolymer is the lack of a large band at  $1300\text{ cm}^{-1}$ , which is characteristic of oxidized polypyrrole.<sup>20</sup> This suggests that isolated polypyrrole chains do not exist in the copolymer nanofibrils and that pyrrole and thiophene monomers are bonded effectively during the polymerization.

Another characteristic is that the bands of the copolymers become more similar to that of polythiophene with the increasing preparation potential, as shown in Figure 7. This indicates that the amount of thiophene units incorporated into the copolymer increases with the increasing preparation potential, which is in accordance with the conclusion of the cyclic voltammetry. Furthermore, another noticeable feature in the spectrum is that an absorption band at around  $790\text{ cm}^{-1}$ , which is characteristic of  $\alpha$ -substituted five-membered heterocyclic compounds,<sup>21</sup> appears in the copolymer, suggesting that the  $\alpha$ -positions of each monomer are involved in copolymerization.

## CONCLUSION

Electrochemical copolymerization of pyrrole and thiophene nanofibrils was conducted successfully using

the template-synthesis method. Copolymer nanofibrils were synthesized in the pores of a microporous AAO membrane. The electron microscopy results showed that the template technique using an AAO membrane can control the length, diameter, and thickness of the copolymer nanofibrils, thus producing uniform and monodisperse copolymer nanofibrils. The electrochemical properties of these nanofibrils were investigated using cyclic voltammetry techniques. The composition of the obtained nanofibrils can also be estimated indirectly using cyclic voltammetry and IR spectroscopy. The result shows that the composition of the copolymer nanofibrils varies with the applied electrochemical polymerization potential: the higher the applied potential is, the more thiophene units that are incorporated into the copolymer nanofibrils.

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